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④ 多層回路板の製造方法

川崎市中原区上小田中1015番地
富士通株式会社内

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⑦ 発 明 者 斎藤和正

② 出 願 昭55(1980)2月22日

川崎市中原区上小田中1015番地

⑧ 発 明 者 猿渡紀男

富士通株式会社内

川崎市中原区上小田中1015番地

⑨ 出 願 人 富士通株式会社

富士通株式会社内

川崎市中原区上小田中1015番地

⑩ 発 明 者 渡辺勲

⑭ 代 理 人 弁理士 松岡宏四郎

明 細 書

1. 発明の名称

多層回路板の製造方法

2. 特許請求の範囲

回路パターンを形成した中間層の両面に酸化銅皮膜を化成し、然るのち一般式 $RSiX_3$ (Rは各種有機官能基をあらわし、Xは珪素原子に結合している加水分解性の基である) によってあらわされるシラン化合物の一種または二種以上のコーティングを施す工程と、この工程により得たプリント回路板に接着用プリプレグシートを重ねて加圧し成形する工程とを含むことを特徴とする多層回路板の製造方法。

3. 発明の詳細な説明

本発明は多層回路板の製造方法に関し、さらに詳しくは多層回路板における層間の接着力を良くした多層回路板の製造方法に関するものである。
多層化を行なう場合、通常内層材とプリプレグとの
従来よりこの種回路板の接着にあたり中間層に
使用する銅箔としてはあらかじめ表面をマット面(鏡面)と同じ程度の粗さにした両面粗化箔を使

用したり、あるいはさらに中間層の銅箔表面に酸化第1銅の皮膜を化成させるため亜酸化銅処理もしくは酸化第2銅の皮膜を化成させるための黒色酸化銅処理法等によって銅箔と前記プリプレグの接着力を補う方法が用いられている。

しかしながら、両面粗化銅箔は通常の片面粗化箔と比べてコストが高く、かつ粗化面の安定化が不充分であり、また中間層の銅箔表面に亜酸化銅処理あるいは黒色酸化銅処理を施す方法はごく一般的に行なわれているものであるが耐塩酸性に劣り酸性液処理後の接着性の低下を生じ、また接着性の低い樹脂たとえばポリイミドやシリコン樹脂にはあまり効果的でないといった問題点があった。

本発明は上記問題点に鑑みなされたものであって、その目的とするところは、スルホールメッキにおいて、メッキ液のしみ込みを防止し、各信号層間の導通の信頼性の向上を得る多層回路板の製造方法を提供することにある。

上記目的達成のため本発明の特徴は回路パター

ンを形成した中間層の両面に、酸化銅皮膜を化成し、然るのち一般式 $RSiX_3$ （ R は各種有機官能基をあらわし、 X は硅素原子に結合している加水分解性の基である）によってあらわされるシラン化合物の一種または二種以上のコーティングを施す工程と、この工程により得たプリント回路板に接着用プリプレグシートを重ねて一体化し、成形したことがある。

本発明において用いられる酸化銅処理は前述の亜酸化銅、無色酸化銅処理が一般的であるが、特に限定するものではない。

又、中間層のコーティングに用いるシラン化合物としては上記一般式であらわされるが、例として γ -グリシドオキシプロピルトリメソキシシラン、 β -（3.4エポキシシクロヘキシル）エチルトリメソキシシラン、 γ -アミノプロピルトリエソキシシラン、 γ -ウレイドプロピルトリエソキシシラン、 γ -クロロプロピルトリメソキシシラン、ビニルトリエソキシシラン等があげられ、適用される樹脂に最も適したシラン化合物が用い

れる。

中間層へのコーティングは上記シラン化合物を1～10%水溶液又はエタノール溶液とし、この溶液中に酸化銅処理後の中間層を浸漬した後50～100℃で乾燥して溶媒を除去する方法がある。

適用し得る基板樹脂としては一般に用いられるエポキシ、ポリエステル等、又、多層層間接着力に比較的劣るポリイミド、シリコン、1,2-ポリブタジエンなど、通常の熱硬化性基板用樹脂があげられ、特に接着力の低い樹脂に最も効果的である。

以下、本発明を実施例で説明する。

実施例1

先ず厚さ0.4mmのエポキシ樹脂の両面銅張板を使用して該銅張板の銅箔表面を水酸化ナトリウム5%+加硫酸カリウム1%、液温100℃の水溶液中に10分間浸漬し煮沸処理を施し、酸化第2銅の皮膜を化成させる。

然るのち、この銅張板を5%の γ -グリシドオキシプロピルトリメソキシシラン（日本ユニカー

製A-187）の水溶液中に浸漬し、100℃で15分間乾燥して水分を除去し、エポキシシランカップリング剤のコーティングを実施する。

このようにして得られた銅張板の上下に厚さ0.1mmのエポキシプリプレグ（松下電工製H1661）を各2枚ずつ合計4枚を重ね合わせ、然るのち170℃に加熱し40kg/cm²の圧力にて60分間の加圧成形を行なう。

この様に加圧成形した多層基板を20×40mmの大きさに切断し、該基板に任意の位置に1.0mm径のドリル孔を10ヶ所あけて試験片を作る。

該試験片を10%塩酸浸漬試験を行ない、液のしみ込み状態を観察することによって耐酸性を調べたその結果、表のごとく液のしみ込みを認めず良好な結果が得られた。

これに対しエポキシ両面銅張板を前記シランカップリング剤（ $RSiX_3$ ）による処理を行なわないで他は全く同様の方法によって多層基板を製作し、同一の寸法の試験片につき同様の塩酸浸漬試験を実施した結果、表に示したごとく30分まで

は液のしみ込みはないが、40分においてしみ込みが認められた。

実施例2

厚さ0.4mmのポリイミド樹脂両面銅張板（松下電工製H4770）の銅箔表面を前記同様の無色酸化銅処理を行ない、次に該銅張板を5%の γ -ウレイドプロピルトリエソキシシラン（日本ユニカー製A1160）の水溶液中に浸漬し、100℃で15分間乾燥し、水分を除去したのちアミノシランカップリング剤のコーティングを施す。

このようにして得た銅張板の両面に0.1mm厚のポリイミドプリプレグ（松下電工製H4670）を2枚ずつ合計4枚を重ね合わせ、然るのち170℃において50kg/cm²で180分間の加圧整形を行なったのち200℃で4時間のアフターキュアを実施する。

然るのち、この多層基板を前記例と同様の試験片に加工し、同様の方法による塩酸浸漬試験を実施した結果、表に示すごとく前記実施例1と同様の液のしみ込みを認めず良好な結果が得られる。

従って、実施例2におけるポリイミド両面銅張板を、シランカップリング剤の処理を行わないでその他は全く同様の方法により多層基板を作製し前記と同一の寸法の試験片を作り、同様の塩酸浸漬試験を実施した結果、下記の表に示す比較例2のごとく20分にて塩酸の浸漬が認められた。

表

浸漬時間(分)	実施例1	比較例1	実施例2	比較例2
10	○	○	○	○
20	○	○	○	×
30	○	○	○	
40	○	×	○	
50	○		○	
60	○		○	

○…合格(液のしみ込みなし)

×…不合格(液のしみ込みにより層間剝離発生)

以上説明したごとく、本発明に係る多層回路板の製造方法であれば回路パターンを形成した中間層の両面に酸化銅皮膜を化成し、然るのちシラン

化合物(RSiX_3)の一種または二種以上のコーティングを施したプリント回路板に、接着用のブリードシートを重ね合わせて一体化し、成形するごとくしたことによりスルホールメッキにおいて別表に示すごとくメッキ液のしみ込みが無く、各信号層間の導通の信頼性の向上を得ることが可能となりその効果は極めて大である。

代理人 弁理士 松岡 宏 四 郎

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SHUSAKU YAMAMOTO

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Name of the Invention: METHOD FOR PRODUCING MULTILAYER
CIRCUIT BOARD

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Name of Inventors: Norio SARUWATARI

Isao WATANABE

Kazumasa SAITO

Name of Applicant Fujitsu Limited

Name of Agent Koshiro MATSUOKA, Patent Attorney

Specification

1. Name of the Invention

METHOD FOR PRODUCING MULTILAYER CIRCUIT BOARD

2. Claims

A method for producing a multilayer circuit board,
comprising the steps of:

forming copper oxide films on both sides of an
intermediate layer, a circuit pattern being provided on the
intermediate layer;

coating the copper oxide films with one or two
or more silane compounds represented by a general formula
 RSiX_3 , where R represents a variety of organic functional
groups; X represents a hydrolyzable group coupled with the
silicon atom); and

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laminating a prepreg sheet on the resultant printed circuit board and applying pressure on the prepreg sheet to form the multilayer circuit board.

2. Detailed Description of the Invention

The present invention relates to a method for producing a multilayer circuit board, and more particularly to, a method for producing a multilayer circuit board in which adhesion between each layer of the multilayer circuit board is enhanced.

A copper foil is typically provided as an intermediate layer used for adhesion between a prepreg and an internal layer in the multilayer circuit board. An attempt to enhance adhesion between the copper foil and the prepreg is conventionally made in the following way. Both sides of the copper foil are made as rough as a matte surface (rear side). Alternatively, a cuprous film is provided on a surface of the copper foil by a cuprous oxide treatment, or a cupric film is provided on a surface of the copper foil by a black copper oxide treatment.

The roughened copper foil roughened on both sides requires more cost, and stability of the roughened sides thereof is insufficient, compared with a typical copper foil roughened on a single side. Moreover, although the cuprous oxide treatment and the black copper oxide treatment are commonly applied to a surface of the copper foil, the copper foil is less resistant to hydrochloric acid and the ability of the copper foil to adhere is decreased after being treated with acid solution. Further, there is a problem in that the copper foil does not very effectively adhere to a resin having less ability to adhere such as a polyimide resin and a silicone resin.

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In view of the above-described problems, an objective of the present invention is to provide a method for producing a multilayer circuit board in which a plating solution is prevented from permeating a plated-through hole, thereby improving reliability of conductance between each signal layer.

To this end, the present invention provides a method for producing a multilayer circuit board which comprises the steps of forming copper oxide films on both sides of an intermediate layer, a circuit pattern being provided on the intermediate layer; coating the copper oxide films with one or two or more silane compounds represented by a general formula RSiX_3 where R represents a variety of organic functional groups; X represents a hydrolyzable group coupled with the silicon atom); and laminating a prepreg sheet on the resultant printed circuit board to form the multilayer circuit board.

As the copper oxide treatment used in the present invention, the above-described cuprous oxide treatment or black copper oxide treatment is typically used. The present invention is not limited to these treatments.

Examples of the silane compound, which is used in the coating of the intermediate layer and is represented by the above-described general formula, includes γ -glycidoxypropyltrimethoxy silane, β -(3,4,epoxycyclohexyl)ethyltrimethoxy silane, γ -aminopropyltriethoxy silane, γ -ureidepropyltriethoxy silane, γ -chloropropyltrimethoxy silane, vinyltriethoxy silane. A silane compound most suitable for a resin material is selected.

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As a method of coating the intermediate layer, an aqueous or ethanol solution containing 1-10% of the above-described silane compound is prepared, and an intermediate layer which has been subjected to the copper oxide treatment is immersed in the solution followed by drying at 50-100°C to remove the solvent.

Examples of an available substrate resin include epoxy, polyester, and the like which are typically used; and polyimide, silicone, 1,2-polybutadiene, and the like which have relatively less adhesion between layers. These are typical thermosetting resins for the substrate which most effectively adhere to a resin having a lesser adhesion force.

Hereinafter, Examples of the present invention will be described.

Example 1

A plate of an epoxy resin having copper foil on both sides thereof and having a thickness of 0.4 mm was prepared. The plate was immersed and boiled in an aqueous solution of 5% sodium hydroxide and 1% potassium persulfate at a liquid temperature of 100°C to form a cupric oxide on the surface of the copper foil of the plate.

Thereafter, the resultant plate was immersed in an aqueous solution having 5% γ -glycidoxypropyltrimethoxy silane (A-187 manufactured by Nippon Unika) followed by drying at 100°C for 15 minutes to remove moisture. The plate was then coated with an epoxy silane coupling agent.

Two pieces of epoxy prepreg (R1661 manufactured by Matsushita Electric Works, Ltd.) having a thickness of 0.1 mm were laminated on each of the upper and lower sides of the plate thus obtained (total four pieces of the epoxy

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prepreg are used). Thereafter, a pressure of 40 kg/cm² was applied to the resultant plate while being heated at 170°C for 60 minutes, thereby forming a multilayer substrate.

The multilayer substrate thus formed was cut and divided into rectangles having a size of 20×40 mm. Ten drilled holes having a diameter of 1.0 mm were provided in each divided substrate at arbitrary positions. The resultant divided substrates are called test pieces.

Each test piece was immersed in 10% hydrochloric acid. Permeation of the solution into the test piece was observed so as to examine resistance to acid. As a result, no permeation of the solution was recognized as indicated in The Table below. Thus, a satisfactory result was obtained.

On the other hand, another multilayer substrate was produced in a similar way, except that the epoxy copper foil plate was not treated by the above-described silane coupling agent (RSiX₃). Test pieces having the same dimension were subjected to a hydrochloric acid immersion test similar to that described above. As a result, permeation of the solution was not observed for first 30 minutes but was observed after 40 minutes as indicated in The Table below.

Example 2

A plate of a polyimide resin (R4770 manufactured by Matsushita Electric Works) having copper foil on both sides and having a thickness of 0.4 mm was prepared. A surface of the copper foil of the plate was subjected to a black copper oxide treatment similar to that described above. Thereafter, the resultant plate was immersed in an aqueous solution having 5% γ -ureidepropyltrimethoxy silane (A-1160 manufactured by Nippon Unika) followed by drying at 100°C

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for 15 minutes to remove moisture. The plate was then coated with an epoxy silane coupling agent.

Two pieces of polyimide prepreg (R4670 manufactured by Matsushita Electric Works, Ltd.) having a thickness of 0.1 mm were laminated on each of the upper and lower sides of the plate thus obtained (total four pieces of the epoxy prepreg are used). Thereafter, a pressure of 50 kg/cm² was applied to the resultant plate while being heated at 170°C for 180 minutes, thereby forming a multilayer substrate. The multilayer substrate was then cured at 200°C for four hours.

Subsequently, from the multilayer substrate thus formed, test pieces were obtained in a similar way to that described in Example 1. The test pieces were subjected to a hydrochloric acid immersion test similar to that described above. Similar to Example 1, permeation of the solution was not observed as indicated in The Table below, thereby obtaining a satisfactory result.

Another multilayer substrate was produced in a similar way, except that the polyimide copper foil plate was not treated by the above-described silane coupling agent. Test pieces having the same dimension were subjected to a hydrochloric acid immersion test similar to that described above. As a result, permeation of the solution was observed after 20 minutes as indicated in The Table below.

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Table

Immersion time (min)	Example 1	Comparative Example 1	Example 2	Comparative Example 2
10	O	O	O	O
20	O	O	O	x
30	O	O	O	
40	O	x	O	
50	O		O	
60	O		O	

O---acceptable (no permeation)

x---not acceptable (peel occurs between layers due to permeation)

As described above, in the method of this invention for producing a multilayer circuit board, the copper oxide film is formed on both sides of the intermediate layer, a circuit pattern being provided on the intermediate layer. The copper oxide films are coated with one or two or more silane compounds (RSiX_3). A prepreg sheet is laminated on the resultant printed circuit board and pressure is applied on the prepreg sheet to form the multilayer circuit board. Thereby, there is no permeation of plating solution in plated-through holes as shown in Table. It is thus possible to improve the reliability of conductance between each signal layer.